PHYSICAL REVIEW B VOLUME 45, NUMBER 20 15 MAY 1992-II

# Cohesive properties of $4d$-transition-metal carbides and nitrides in the NaCl-type structure

A. Fernández Guillermet
*Consejo Nacional de Investigaciones Científicas y Técnicas, Centro Atómico Bariloche, 8400 San Carlos de Bariloche, Argentina*

J. Häglund and G. Grimvall
*Department of Theoretical Physics, The Royal Institute of Technology, S-100 44 Stockholm, Sweden*

(Received 23 August 1991; revised manuscript received 2 January 1992)

We present a study of the cohesive energies ($E_{\rm coh}$) of all $4d$-transition-metal carbides and nitrides in the NaCl-type structure using *ab initio* linear-muffin-tin-orbitals type total-energy calculations and an extensive analysis of thermodynamic data. Many of the carbides considered here are metastable and their cohesive energy is not known from direct measurements. In these cases, we estimate $E_{\rm coh}$ using thermodynamic model calculations and analyses of phase diagrams. This information allows us to perform a detailed comparison of theoretical ($E^{\rm th}_{\rm coh}$) and thermodynamic ($E^{e}_{\rm coh}$) cohesive energy values. The difference $E^{\rm th}_{\rm coh} - E^{e}_{\rm coh}$ is positive for all carbides and nitrides, and we discuss the various sources of error in the theoretical approach. Trends in theoretical $E_{\rm coh}$ values are remarkably improved when spectroscopic data are used to correct calculated atomic total energies. We also show that most of the discrepancy between theoretical and thermodynamic results cancels in the difference $\Delta E_{\rm coh}$ between a carbide $M$C and a nitride $M$N of the same transition-metal $M$, and excellent agreement with experiments is obtained for the systems where thermodynamic information is available, viz., for $M$=Zr, Nb, and Mo. This fact allows us to estimate the unknown cohesive energies and enthalpies of formation for YN, TcN and for the metastable NaCl structures of RuN, RhN, and PdN, from a combination of *ab initio* results and assessed thermodynamic information for the corresponding carbides. Our method of theory-based predictions of thermodynamic quantities is compared with the semiempirical method of Miedema. We also discuss the role of extrapolation methods related to *ab initio* results in the estimation of thermodynamic information that is used in the modeling of alloy phase diagrams.

## I. INTRODUCTION

In this paper we shall be interested in bonding properties of solids, in particular *ab initio* values for cohesive energies and enthalpies of formation as input parameters in phase-diagram calculations. Theoretical metallurgists and materials scientists have developed an elaborate combination of databases with computer programs and assessed thermodynamic information to calculate phase diagrams of, e.g., binary, ternary, and higher-order alloy systems.[1] Such calculations are very demanding on the accuracy of the input information, which usually is taken from experiments. Compared with experimental work, *ab initio* calculations are very quick and cheap. A strong motivation for this paper is to investigate to what extent such band-structure results can be useful, e.g., as input in phase-diagram calculations when no direct experimental data are available.

In order to test our expectations about the possible use of *ab initio* and thermodynamic information, we have studied the cohesive energy $E_{\rm coh}$ of all $4d$-transition-metal carbides and nitrides, $M$C and $M$N, in the NaCl-type structure using both linear-muffin-tin-orbitals (LMTO) electron-structure calculations and an analysis of experimental data. In previous studies[2,3] of several of the corresponding $3d$-transition-metal compounds, we have found strong regularities in bonding properties which can to a first approximation be described by electron-band-filling arguments. Gelatt, Williams, and Moruzzi[4] have also performed *ab initio* calculations of the cohesive properties of NaCl-type structure carbides and nitrides of the $4d$-transition-metals. Their emphasis is on the contribution of various electron states to the bonding properties, and no direct comparison with experiments is made. In our case, we focus on a comparison between theory and experiment and therefore, we have carried out an extensive analysis of direct and indirect experimental thermodynamic information.

The cohesive energies of most stable carbides considered here are relatively well known from experiments, and the cohesive energies of the metastable carbides will be derived by us using thermodynamic methods and phase diagram information. The information so obtained, which is also interesting in itself, allows us to perform a detailed comparison between LMTO and thermodynamic $E_{\rm coh}$ values for all $M$C compounds. The properties of the corresponding nitrides are in general less known and we predict their $E_{\rm coh}$ using the *ab ini-*

*tio* information. We also derive the room-temperature enthalpy of formation, a quantity that is relevant both in phase-diagram calculations and in the interpolation scheme developed by Miedema and his co-workers[5]. The predictions of their scheme have often been tested using experimental information on stable compounds. In the present work, we shall extend appreciably such a test of Miedema's approach by including compounds that have not been studied by direct experimental methods.

Because of the discrepancies between *ab initio* and thermodynamic values that are known for simple substances (e.g., on the magnitude of the zero-Kelvin enthalpy difference between the bcc, fcc, and hcp structures of the transition metals[6–9]) there has been no significant coupling to *ab initio* results in the assessment of thermodynamic information to be used in phase-diagram calculations. These assessments have traditionally been carried out by purely thermodynamic methods, relying on measurements. We shall comment on the role of total-energy calculations as a complement to experimental data, both in a theory-based interpolation and extrapolation procedure, and as a useful guide in assessing the reliability of existing estimates.

The plan of the paper is as follows. In Sec. II we describe the computational methods of our theoretical approach and in Sec. III we explain how the assessment of cohesive energies from thermodynamic information has been carried out. In Sec. IV we present our results and in Sec. V we discuss the accuracy and the sources of errors in the theoretically determined cohesive-energy values, and then predict unknown enthalpy-of-formation values for metastable nitrides. Section V also contains a comparison of our enthalpy-of-formation values with the predictions of the approach of Miedema and co-workers.[5] In Sec. VI, we comment on the possible application of our results in thermodynamic modeling of phase diagrams. The paper ends with conclusions in Sec. VII.

## II. THEORETICAL

The theoretical cohesive energies $E^{\mathrm{th}}_{\mathrm{coh}}$ presented in this work were calculated as the difference between the total electronic energies of the compound ($MX$) and of its constituent atoms ($M$,$X$):

$$E^{\mathrm{th}}_{\mathrm{coh}} = -\left(\tfrac{1}{2}\right)\left(E_{MX} - E_M - E_X\right). \tag{1}$$

The total electronic energies of the compounds were determined from self-consistent band-structure calculations. These were performed using the linear-muffin-tin-orbitals method[10] (LMTO), and the local-spin-density (LSD) parametrization of Gunnarsson-Lundqvist was adopted. The calculations were carried out for a 505-**k**-point mesh in an irreducible wedge of the Brillouin zone. The basis set was chosen to contain $s$, $p$, $d$, and $f$ states for the metal atoms and $s$, $p$, and $d$ states for the nonmetal atoms. The lattice parameters $a_0$ were set to experimental (directly measured or extrapolated) values for the stoichiometric composition of all stable compounds, while extrapolation and interpolation procedures were used to estimate lattice parameters for the metastable compounds in the series (cf. Sec. III). All these values are listed in Tables I and II. We expect our *ab initio* calculations to be reliable for determining the ground-state properties of the $4d$-transition-metal $MX$ carbides and nitrides in the NaCl structure.

The total electronic energies of the *atoms* are obviously as important for the calculation of cohesive energies as are the total electronic *bulk* energies. Although the computational effort to determine atomic energies is much smaller than in the bulk case, it is likely that a significant part of the errors in the cohesive energies originates from the atomic calculation. The problem is complicated by the fact that the entire concept of determining bulk and atomic energies separately relies on important cancellations of systematic errors in the subtraction in Eq. (1). The atomic program, used in this paper,[3] was designed to maximize these cancellations. This is achieved by using the same numerical routines and the same LSD parametrizations in both cases. However, the fact that the density regime in the free atom contains the limit of low density (which is not covered in the solid), prevents a cancellation of LSD errors for this density (or spatial) range. The idea of treating a spherically averaged charge distribution and thus to iterate a spherically symmetric muffin-tin (MT) potential is also retained in the atomic case. There are several reasons why the LSD and the MT approximations may be less accurate in the atomic than in the bulk case. This is reflected by the fact that atomic valence-electron configuration which minimizes the total electronic energy, in many compounds differs from the experimental configuration[3]. The origin of errors in the atomic energies, and to what extent they may influence the accuracy of the cohesive energies, will be discussed in Sec. V.

## III. COHESIVE ENERGY FROM EXPERIMENTAL INFORMATION

### A. Definitions and thermodynamic relations

The experimental analogue $E^{e}_{\mathrm{coh}}$ of the quantity $E^{\mathrm{th}}_{\mathrm{coh}}$ defined by Eq. (1) is the enthalpy change per atom for the reaction

$$MX(\mathrm{st}) \rightarrow M(g) + X(g) \tag{2}$$

at zero Kelvin and one atmosphere, viz.,

$$E^{e}_{\mathrm{coh}} \equiv -\left\{ \tfrac{1}{2}\left[{}^{0}H^{\mathrm{st}}_{MX}(0) - {}^{0}H^{g}_{M}(0) - {}^{0}H^{g}_{X}(0)\right] - \tfrac{9}{8}k_B\Theta^{C}_{MX}\right\}. \tag{3}$$

${}^{0}H^{\mathrm{st}}_{i}(0)$ and ${}^{0}H^{g}_{i}(0)$ represent the enthalpy at zero Kelvin and one atmosphere per formula unit of the substance $i$ ($i = MX, M, X$) in its stable (st) modification and in the gaseous ($g$) monatomic state, and $\frac{9}{8}k_B\Theta^{C}_{MX}$ corrects[3] for the zero-point vibrational energy per atom of $MX$. The right-hand side in Eq. (3) is expressed[3] in terms of quantities that are given in standard compilations of thermodynamic data, or have been estimated. We get

$$E^{e}_{\text{coh}} = -\Big( \tfrac{1}{2}\{\Delta^0 H^{\text{st}}_{MX}(T_0) - \Delta H_0^{T_0} - [\Delta^0 H_M^{\text{st}\to g}(0) + \Delta^0 H_X^{\text{st}\to g}(0)]\} - \tfrac{9}{8} k_B \Theta^{C}_{MX} \Big), \tag{4}$$

where $\Delta^0 H^{\text{st}}_{MX}(T_0)$ is the enthalpy of formation of the compound $MX$ from the elements in their stable modifications at one atmosphere and $T_0$ = 298.15 K. This quantity is available from direct measurements in sta-

TABLE I. Average number of valence electrons per atom ($n_e$), lattice parameter ($a_0$), room-temperature enthalpy of formation $[\Delta^0 H^{\text{st}}(T_0)]$, Debye temperatures ($\Theta$), and cohesive energy ($E_{\text{coh}}$) of NaCl-type structure carbides of the 4$d$ transition metals. $E^{\text{th}}_{\text{coh}}$ and $E^{e}_{\text{coh}}$ denote cohesive energy values derived from LMTO calculations and based on thermodynamic information, respectively. The values in parentheses are our estimates of the probable uncertainty.

| Compound | $n_e$ ($e/a$) | $a_0$ (a.u.) | $\Delta^0 H^{\text{st}}(T_0)$ (kJ/mol $a$) | $\Theta^C$ (K) | $\Theta^S$ (K) | $E^{e}_{\text{coh}}$ (mRy/$a$) | $E^{\text{th}}_{\text{coh}}$ (mRy/$a$) |
|---|---|---|---|---|---|---|---|
| YC | 3.5 | 9.817[a] | −46 (± 11)[b] | | 523[c] | 470 (± 11) | 544 |
| ZrC | 4.0 | 8.878[d] | −103.6 (± 3)[e] | 624 (± 13)[f] | 650[g] | 583 (± 7) | 682 |
| NbC | 4.5 | 8.447[h] | −70.3 (± 3)[i] | 660 (± 40)[j] | 634[g] | 607 (±7) | 669 |
| MoC | 5.0 | 8.084[k] | −6.3 (± 4)[l] | | 616[c] | 531 (± 7) | 580 |
| TcC | 5.5 | 7.905[m] | 32 (± 6)[n] | | 578[c] | 506 (± 11) | 581 |
| RuC | 6.0 | 7.803[o] | 37 (± 9)[p] | | 554[c] | 495 (± 10) | 570 |
| RhC | 6.5 | 7.833[o] | 36 (± 6)[q] | | 514[c] | 458 (± 8) | 537 |
| PdC | 7.0 | 7.976[o] | 32 (± 6)[r] | | 483[c] | 394 (± 8) | 435 |

[a] Our extrapolation, assuming a linear variation of $a_0$ for Y(C,$V$) with the atomic fraction of C. $a_0$ for Y($V$) was estimated by us from lattice parameter data (Ref. 39), and $a_0$ for Y($C_{0.25}V_{0.75}$) and Y($C_{0.4}V_{0.6}$) was from direct measurements (Ref. 40).

[b] Based on measurements of $\Delta^0 G$ for Y carbides in the NaCl structure (Ref. 41). A smooth graphical interpolation between the measured values gives $\Delta^0 G_{\text{YC}} = (-50 \pm 1)$ kJ/mol of atoms. This value, combined with our description of the thermal functions, and with $\Theta^S(T) = \Theta^S - 0.10(T - \Theta^S)$ as in Ref. 21 yields $\Delta^0 H = -46$ kJ/mol of atoms. Neglecting the temperature dependence of $\Theta^S$ yields $\Delta^0 H = -57$ kJ/mol of atoms. The uncertainty given in Table I expresses the difference between those calculations.

[c] Estimated value, Sec. III B.

[d] Reference 42.

[e] Reference 43.

[f] Reference 44.

[g] Reference 45.

[h] References 46 and 47.

[i] Reference 48.

[j] Based on a measurement (Ref. 44) for $\text{NbC}_{0.93}$ and an account of the effect of nonstoichiometry upon $\Theta^C$ based on experiments (Ref. 49) for the range $\text{NbC}_{0.77}$–$\text{NbC}_{0.96}$.

[k] Reference 50.

[l] Extrapolated value from a thermodynamic analysis of the Mo-C system (Ref. 51) using the two-sublattice model (Ref. 25).

[m] Estimated value. It refers to the stoichiometric composition, and is about 5% larger than values reported (Refs. 52 and 53) for Tc(C,$V$) carbides based on an fcc arrangement of Tc atoms.

[n] Based on our analysis of the phase equilibria in the Tc-C system using the two-sublattice model (Ref. 25) and experimental information (Refs. 53–56).

[o] Estimated, by extrapolation of $\Omega_{MC}$ for carbides of other 4$d$ transition metals, and based on the analogous variations in plots of $\Omega_{MC}$ and $\frac{1}{2}\Omega_M$ vs the position of $M$ in the Periodic Table.

[p] From our analysis of the Ru-C phase diagram using the two-sublattice model (Ref. 25). The metastable stoichiometric NaCl-structure compound RuC was treated using $\Theta^S$ from Table I and $\Delta^0 H^{\text{st}}_{\text{RuC}}$ was varied until the observed metastability was reproduced. That yielded $\Delta^0 H^{\text{st}}_{\text{RuC}} > 20.1$ kJ/mol atoms. The final estimate of $\Delta^0 H^{\text{st}}_{\text{RuC}}$ was obtained from calculations of the equilibria involving the metastable interstitial phase Ru(C,$V$), graphite, and liquid. The liquid phase was described using parameters such that the experimental information on the (stable) hcp+liquid+graphite three-phase equilibrium (Refs. 56 and 57) was reproduced. With Ru(C,$V$) according to Table I one then obtains a metastable fcc+liquid+graphite three-phase equilibrium temperature $T_e \approx 1900$ K. This value falls in the range 1800 K $\leq T_e \leq$ 2000 K estimated for Ru-C by an interpolation procedure based on $T_e$ for Tc-C ($T_e$=2108 K calculated by us, see above) and Rh-C [$T_e$=1947 K, from experiments (Ref. 57)] and on the trends in $T_e$ for Mn-C (Ref. 58), Fe-C (Ref. 59), and Co-C (Ref. 60). The uncertainty given to $\Delta^0 H^{\text{st}}_{\text{RuC}}(T_0)$ in Table I corresponds to a probable uncertainty of ±100 K in $T_e$.

[q] From a thermodynamic analysis of the Rh-C phase diagram comprising the solubility of C in fcc Rh (Ref. 56) and the fcc+liquid+graphite three-phase equilibrium temperature (Ref. 57).

[r] As in q, using information on the solubility of C in fcc Pd (Ref. 61) and the fcc+liquid+graphite three-phase equilibrium temperature (Ref. 56).

ble compounds and was estimated for metastable compounds, see below. $\Delta H_0^{T_0}$, defined as

$$\Delta H_0^{T_0} \equiv [{}^0H_{MX}^{\rm st}(T_0) - {}^0H_{MX}^{\rm st}(0)] - [{}^0H_M^{\rm st}(T_0) - {}^0H_M^{\rm st}(0)] \\ -[{}^0H_X^{\rm st}(T_0) - {}^0H_X^{\rm st}(0)] \qquad (5)$$

accounts for the enthalpy difference between temperatures 0 and $T_0$. It can be taken directly from thermodynamic measurements for the elements $M$ and $X$ (Refs. 11-17) and for stable $MX$ compounds. For metastable compounds ${}^0H_{MX}^{\rm st}(T_0) - {}^0H_{MX}^{\rm st}(0)$ was estimated[3] using the Debye model with an estimated Debye temperature $\Theta_{MX}$ (see below) and neglecting nonvibrational and anharmonic contributions. $\Delta^0H_M^{{\rm st}\to g}(0)$ and $\Delta^0H_X^{{\rm st}\to g}(0)$ in Eq. (4) represent the atomization enthalpies of the elements $M$ and $X$ at zero Kelvin and one atmosphere. They were taken from compilations of thermodynamic data for the elements.[13,18–20]

### B. Extrapolation methods for $\Theta_{MX}^S$ and $\Delta^0H_{MX}$ of metastable phases

In the $M$-C systems with $M$=Ru, Rh, and Pd the stable phase diagram contains only the metal-rich solution of C in $M$ and graphite as solid phases, and the $M$C carbides involving those metals will be referred to as metastable. The stable phase diagram of the corresponding $M$-N systems has not been established experimentally, but the NaCl-structure compounds RuN, RhN, and PdN do not seem to have been detected, and we also refer to these compounds as metastable. Our estimation procedures for thermodynamic properties of metastable compounds, discussed in detail elsewhere,[21] rely on thermodynamic models for the calculation of phase diagrams. The main points are as follows. Knowing the molar Gibbs energy $G_m$ of all competing phases in a system as a function of temperature and composition one can calculate the phase diagram by standard thermodynamic methods.[22] $G_m$ for stable phases (e.g., $M$, graphite) is available from descriptions based on direct measurements, but $G_m$ of metastable phases has to be estimated. Since $G = H - TS$ we need at least two quantities, representing the enthalpy and the entropy, to characterize the properties of a metastable $MX$ compound. The entropy at high temperatures was modeled by an entropy Debye temperature[23] $\Theta_{MX}^S$ which is available for stable phases from the experimental vibrational entropy at high temperatures. $\Theta_{MX}^S$ for metastable phases was estimated

TABLE II. Average number of valence electrons per atom ($n_e$), lattice parameter ($a_0$), room-temperature enthalpy of formation [$\Delta^0H^{\rm st}(T_0)$], Debye temperatures ($\Theta$), and cohesive energy ($E_{\rm coh}$) of NaCl-type structure nitrides of the 4$d$ transition metals. $E_{\rm coh}^{\rm th}$ and $E_{\rm coh}^{e}$ denote cohesive energy values derived from LMTO calculations and based on thermodynamic information, respectively. $E_{\rm coh}^{e}$ and $\Delta^0H^{\rm st}(T_0)$ values in italics were obtained by applying a predictive method which makes use of the theoretical results (Sec. V B). The remaining $E_{\rm coh}^{e}$ and $\Delta^0H^{\rm st}(T_0)$ were obtained from purely thermodynamic methods. The values in parentheses are our estimates of the probable uncertainty.

| Compound | $n_e$ ($e/a$) | $a_0$ (a.u.) | $\Delta^0H^{\rm st}(T_0)$ (kJ/mol $a$) | $\Theta^C$ (K) | $\Theta^S$ (K) | $E_{\rm coh}^{e}$ (mRy/$a$)[e] | $E_{\rm coh}^{\rm th}$ (mRy/$a$) |
|---|---|---|---|---|---|---|---|
| YN | 4.0 | 9.240[a] | *−224* (*± 20*)[b] | | 607[c] | *513* (*± 15*) | 587 |
| ZrN | 4.5 | 8.649[d] | −185.2 (± 3)[e] | 649[f] | 582[g] | 553 (± 5) | 651 |
| NbN | 5.0 | 8.300[h] | −118.8 (± 3)[i] | 510[j] | 539[c] | 551 (± 5) | 604 |
| MoN | 5.5 | 7.963[k] | −31.2 (± 4)[l] | | 486[c] | 456 (± 5) | 494 |
| TcN | 6.0 | 7.772[m] | *45.0* (*± 14*)[b] | | 446[c] | *403* (*± 11*) | 478 |
| RuN | 6.5 | 7.668[n] | *79.6* (*± 14*)[b] | | 416[c] | *369* (*± 11*) | 447 |
| RhN | 7.0 | 7.714[n] | *54.0* (*± 14*)[b] | | 392[c] | *351* (*± 11*) | 430 |
| PdN | 7.5 | 7.833[n] | *38.6* (*± 14*)[b] | | 371[c] | *296* (*± 11*) | 337 |

[a] Reference 62.

[b] Present prediction, Sec. V B.

[c] Estimated value, Sec. III B.

[d] Reference 63.

[e] Obtained by combining the average of two determinations (Refs. 64 and 65) of the enthalpy of combustion of ZrN, with the enthalpy-of-formation value for $ZrO_2$ (Ref. 66) adopted (Ref. 43) in the evaluation of $\Delta^0H$ for ZrC.

[f] Reference 67.

[g] Reference 45.

[h] Reference 68.

[i] Reference 64.

[j] Reference 67.

[k] Based on combining $a_0$ for Mo nitrides with 28.6 at. % and 34.4 at. % (Ref. 69) and 27.5 at. % (Ref. 70) and a measurement for 50 at. % N (Ref. 71) and assuming a linear variation in $a_0$ with the atomic fraction of N.

[l] Extrapolated value, based on a analysis of the Mo-N system (Ref. 72) using the two-sublattice model (Ref. 25).

[m] Our estimate. Reference 73 studied Tc nitrides of various Tc:N contents, up to 43 at. % N, and reported $a_0$ varying from 7.521 a.u. to 7.531 a.u. Our estimate for the stoichiometric TcN is larger, but fits smoothly the variation of $\Omega_{MN}$ for other $M$N compounds as a function of the position of $M$ in the Periodic Table.

[n] Estimated by extrapolation of $\Omega_{MN}$ for nitrides of other 4$d$ transition metals, cf. RuC.

from the quantity $E_S$, defined as

$$E_S = \left(\frac{k_B \Theta^S_{MX}}{\hbar}\right)^2 M_{\text{eff}}\, \Omega_{MX}^{2/3} . \tag{6}$$

$M_{\text{eff}}$ is the logarithmic average of the atomic masses, and $\Omega_{MX}$ is the average volume per atom of the compound. Previous studies of various carbides,[2,21] nitrides,[2] and borides[24] with the same crystal structure have shown a large degree of regularity in $E_S$, which allowed the estimation of $E_S$ (and therefrom $\Theta^S$) for a compound by using the known $E_S$ of a related compound. All estimations of $\Theta^S_{MX}$ in the present work were based on known $\Theta^S$ values for the NaCl-structure compounds ZrC, ZrN, and NbC, and on graphical extrapolations in plots of $E_S$ vs the average number of valence electrons per atom $n_e$ while being guided by the behavior of $E_S$ for the corresponding $MX$ compounds of the 3*d*-transition-metal series.[2,21] Tables I and II give our estimated $\Theta^S_{MX}$ and also some Debye temperatures $\Theta^C_{MX}$ obtained from low-temperature experiments. Lacking $\Theta^C_{MX}$ values for metastable phases we take $\Theta^C_{MX} = \Theta^S_{MX}$ when estimating their zero-point energies [Eq. (3)] and the ${}^0H^{\text{st}}_{MX}(T_0) - {}^0H^{\text{st}}_{MX}(0)$ difference in Eq. (5).

The remaining parameter in $G_m$ of a metastable $MX$ phase, viz., the room-temperature enthalpy of formation $\Delta {}^0H^{\text{st}}_{MX}$, was obtained by analyzing phase-diagram information on the $M$-C systems ($M$=Tc, Ru, Rh, Pd) using the two-sublattice model[25] for interstitial phases. The NaCl (cF8) structure may be represented by two interpenetrating fcc (cF4) sublattices, one formed by the metallic $M$ atoms and one by C atoms and vacant ($V$) interstitial sites. When the second sublattice is fully occupied with C atoms, one has the stoichiometric $M$C compound. If all C sites are vacant one obtains the $M$ metal in the fcc structure. The two-sublattice model requires that one knows $G_m$ for pure fcc $M$ and for $M$C (cF8). For intermediate C contents the phase is represented as $M$(C,$V$), and $G_m$ is treated using a regular-solution type of model with a phenomenological parameter $L$ accounting for the interaction between the vacant interstitial sites ($V$) and the C atoms. To model $G_m$ of $M$C (cF8) ($M$=Tc, Ru, Rh, Pd) we used $\Theta^S_{MC}$ from Table I and determined $L$ and $\Delta {}^0H^{\text{st}}_{MX}$ by performing fits[26] to experimental phase-equilibrium data. The properties of YC were evaluated from measurements of the Gibbs energy of formation, $\Delta^0 G$ for Y carbides with the NaCl structure. A survey of the sources of information is given in Table I. A detailed account of our extrapolations and estimates is given elsewhere[27] and is available on request. Finally, we emphasize that the values of $a_0$ and $\Delta {}^0H^{\text{st}}_{MX}(T_0)$ presented in Tables I and II correspond to $M$C and $M$N compounds with the stoichiometric composition, and that the uncertainty in the extrapolation to stoichiometry is included in the error limits given by us.

## IV. RESULTS

The cohesive energy values obtained in the present study are summarized in Figs. 1(a) and 1(b). The theoretical cohesive energies ($E^{\text{th}}_{\text{coh}}$) obtained as described in Sec. II, are represented by the upper curves in Fig. 1. The thin lines show how the theoretical cohesive energy values change when the atomic energies are corrected using spectroscopic data (see below). The full-drawn lower curves represent the values from thermodynamic information ($E^{e}_{\text{coh}}$), whereas the dashed part of the lower curve for nitrides refers to $E_{\text{coh}}$ obtained by a predictive method which makes use of the theoretical results (Sec. V B).

There is a general agreement between the trends of the theoretical and thermodynamic values, which encourages an interpretation of the variation in $E_{\text{coh}}$ based on the electronic density of states (DOS) and band-filling arguments. As examples of the electronic density of states in the series of 4*d*-transition-metal carbides and nitrides, we plot the DOS curves for MoC and NbN in Figs. 2 and 3. The similarity of these two curves is typical for the compounds studied in this paper (except for YN, see below), and rigid-band arguments should be valid.

The central part of the DOS (Figs. 2 and 3) is characterized by two regions of high DOS separated by a low-density region. The lower peak arises from the hybridization of *p* and *d* states, and the upper peak is dominated by *d* states. The minimum between these two regions separates bonding and antibonding *p*-*d* states. This fact

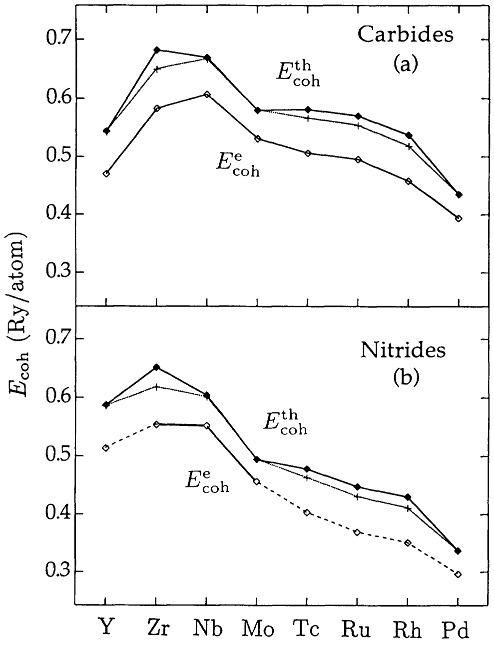

FIG. 1. The cohesive energy $E_{\text{coh}}$ of (a) carbides and (b) nitrides of the 4*d*-transition-metal series obtained in the present study. Filled symbols connected by a solid line refer to theoretical values, and empty symbols connected by a solid line refer to values derived from thermodynamic information. Empty symbols connected by a dashed line refer to values derived in Sec. V B by combining thermodynamic and theoretical results. Crosses connected by a thin line represent theoretical $E_{\text{coh}}$ values obtained when the atomic energy has been corrected using experimental, spectroscopic data.

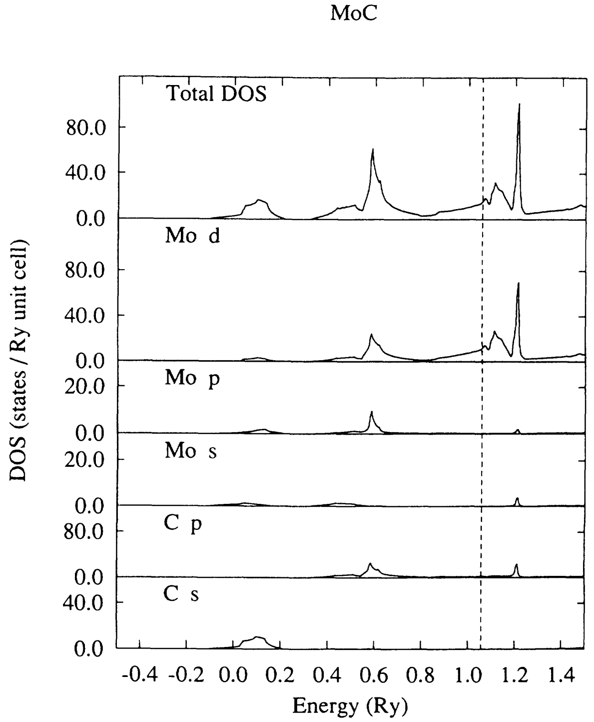

FIG. 2. Electronic density of states of MoC.

is generally[2,4] used to explain the maximum in the $E_{\mathrm{coh}}$ curve for compounds having the Fermi level close to this depletion in the DOS.

An analysis of the discrepancy between theoretical and thermodynamic $E_{\mathrm{coh}}$ values and a discussion of errors in the theoretical approach follows in Sec. V A. Here we shall comment on the fact that the theoretical curve places the maximum in $E_{\mathrm{coh}}$ on ZrC and ZrN in the carbide and nitride series, respectively, while experimental data show that NbC has the highest cohesive energy in the carbide series and that ZrN and NbN have almost equal $E_{\mathrm{coh}}$ values. We believe that this difference is mainly due to an error in the calculated total energy of the Zr atom. This possibility is strongly supported by the thin lines in Fig. 1, which show cohesive energies obtained when the atomic energies have been corrected[28,29] using experimental, spectroscopic data[30] in those cases where the LSD approximation predicts the wrong ground-state electronic configuration. For the Zr atom, the LSD approximation predicts the configuration $(4d\uparrow)^3 5s\uparrow$,[3] which can be described as a weighted average over the two lowest-lying quintets $^5F$ and $^5P$ in the atomic spectrum of Zr. This average is 65.2 mRy above the experimental ground-state energy and the LSD result should be corrected by this amount. Further, we note that also for Tc, Ru, and Rh, for which the atomic energies are lowered by 29.9, 32.6, and 36.5 mRy, respectively, the correction leads to a significant reduction of the discrepancy between theoretical and thermodynamic $E_{\mathrm{coh}}$ values.

The electronic structure of YN differs from that of the other compounds in the series (Fig. 4). A band gap with the width 0.12 Ry (1.7 eV) opens up between bonding and antibonding $p$-$d$ states. This is in analogy with results from our previous calculations on the corresponding carbides and nitrides of the $3d$ transition metals[3,31] where

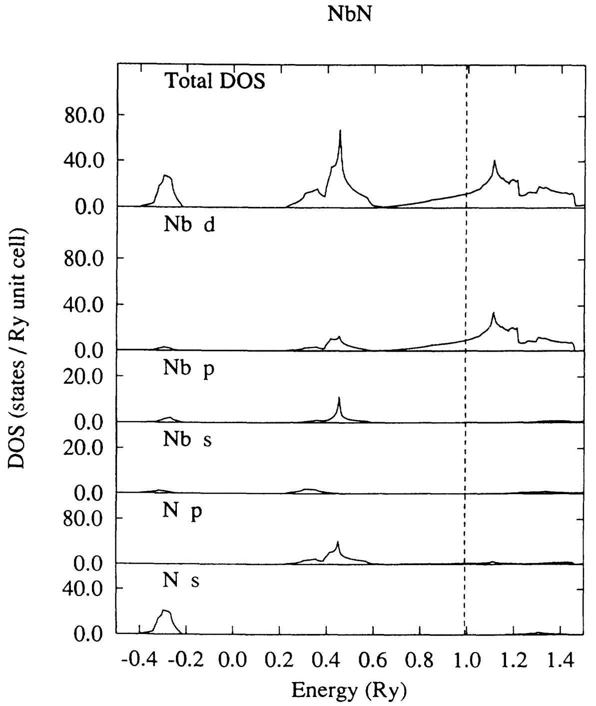

FIG. 3. Electronic density of states of NbN.

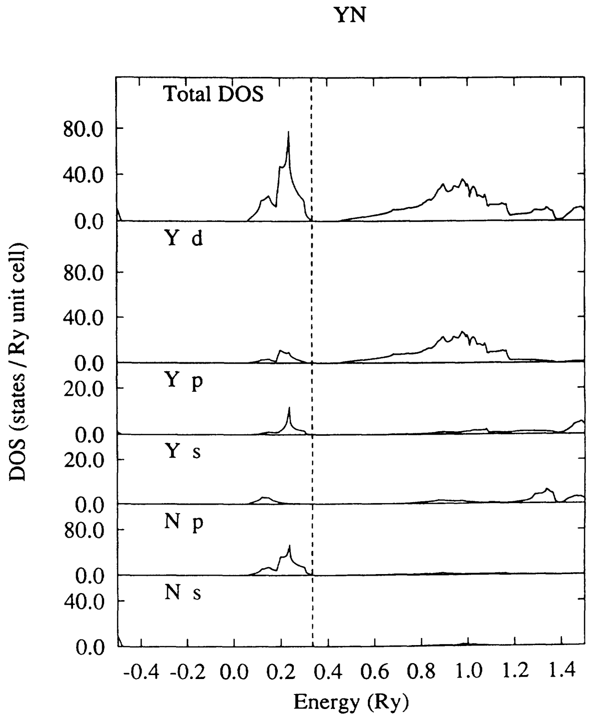

FIG. 4. Electronic density of states of YN.

ScN alone was predicted to have a band gap at the Fermi level.

## V. DISCUSSION

### A. Sources of errors in the *ab initio* calculations

In the previous section we found that the theoretical cohesive energies are larger than the experimental values. These differences, which vary between 41 and 99 mRy in the carbide series, are much larger than the uncertainties in the thermodynamic values obtained in Sec. III (7–11 mRy), and one must conclude that they are mainly due to errors in the theoretical approach. We now study the possible sources of these errors by examining the major approximations that are used. In particular, we pay attention to whether the approximations contribute to a constant, systematic shift between theoretical and experimental cohesive energies, or if they contain a nonsystematic part that varies significantly through the series of compounds.

The fact that we calculate total bulk energies at the experimental (or estimated) $a_0$ instead of first minimizing the energy with respect to the lattice parameter does not affect our results by more than 2 mRy.

A major part of the discrepancy between experimental and theoretical cohesive energies for transition metals and their compounds is generally ascribed to the LSD approximation,[32] which is used in the calculation of both the bulk and the atomic total energies. For the metallic systems considered in this work, where the electronic charge density remains high in the interstitial region of the crystal, there is no obvious reason for the failure of the LSD approximation in the bulk case. However, in the atomic case, the LSD functional is used not only in the vicinity of the nucleus, but also in the distant region where the charge density falls off towards zero. In this region, two important errors are made: Firstly, the exchange and correlation part of the density functional is retained, although a decaying charge density should leave a correlation hole of charge +1 behind, and therefore a different potential. Secondly, certain atoms with only one spin direction in the valence configuration[3] will have a relative spin density close to one in the region far from the nucleus since the contribution to the charge density from core electrons is negligible. This regime of extreme polarization is poorly tested in the LSD approximation. Whereas the error from the first of these effects can be expected to vary smoothly in the transition-metal series, since no drastic changes in the total charge density occurs, the second effect will influence mostly those atoms with large differences in spin-up and spin-down occupation in the atomic valence configuration [e.g., Cr and Mo (Ref. 3)]. This will therefore affect the nonsystematic part of the error in the total atomic energy, $E_M$.

The second major approximation made in our theoretical calculations is the muffin-tin-potential approximation, which implies that a spherically symmetric potential is iterated to self-consistency. In the bulk case, this approximation is best adopted for close-packed structures, e.g., the NaCl structure. The situation in the atomic case is quite different. Since the experimental atomic valence-electron configuration of some atoms reduces to a spherical charge distribution, e.g., for the Mn atom, the treatment of a spherically symmetric potential is exact for these systems. However, in other cases, the use of a muffin-tin potential implies that the atomic total energy is calculated for a charge distribution corresponding to an average over several multiplets.[29] This will yield a total electronic energy that is higher than the ground state and thus contributes to an overestimation of the cohesive energy. This effect can be successfully compensated for by using experimental information on the atomic energy spectrum, cf. Sec. IV.

In conclusion, it is not unexpected that the cohesive energies of the 4*d*-transition-metal carbides and nitrides are overestimated in our theoretical calculations since the approach is better suited for determining the ground-state properties of the compounds (*MX*) than of their constituent atoms (*M*,*X*). Furthermore, in line with the results in Fig. 1, we expect that most of the nonsystematic part of the error in $E^{\mathrm{th}}_{\mathrm{coh}}(MX)$ should be contained in the total energy of the transition-metal atom ($E_M$).

### B. Theory-based predictions of $E_{\mathrm{coh}}$ and $\Delta^0H^{\mathrm{st}}$

The main purpose of the present work is to investigate to what extent *ab initio* calculations are capable of generating, directly or indirectly, information of practical interest in thermodynamic calculations at high temperatures. Current calculations on *MX* (*X*=C,N) and more complex systems often require information on $\Delta^0H^{\mathrm{st}}(T_0)$ for stable and metastable *M*C and *M*N NaCl-structure compounds (cf. Sec. VI). Here we study how the theoretical results of Sec. IV can be used to generate reliable enthalpy values for 4*d*-transition-metal nitrides.

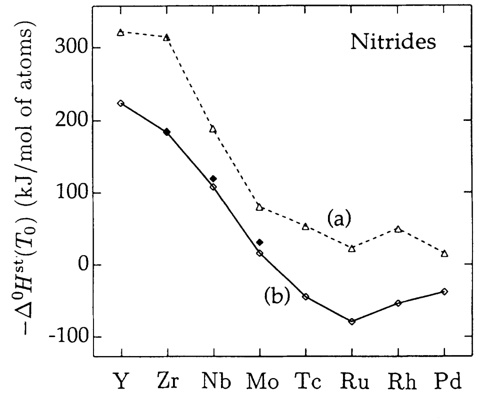

FIG. 5. The enthalpy of formation $\Delta^0H^{\mathrm{st}}$ of NaCl-structure nitrides of the 4*d*-transition-metal series according to our assessment of thermodynamic information on ZrN, NbN, and MoN (filled symbols) and to two predictive approaches that make use of the theoretical results (empty symbols). Empty triangles connected by a dashed line labeled (a) represent $\Delta^0H^{\mathrm{st}}(T_0)$ values obtained by applying Eq. (7), and empty diamonds connected by the solid line labeled (b) show values predicted from Eq. (8).

The simplest approach to estimate enthalpies would be to combine the theoretical $E_{\mathrm{coh}}$ values for $M$N with experimental information about $M$ and N, and derive $\Delta^0 H^{\mathrm{st}}$ using the standard relation given in Sec. III A, i.e., assuming

$$E^{e}_{\mathrm{coh}}(M\mathrm{N}) = E^{\mathrm{th}}_{\mathrm{coh}}(M\mathrm{N}). \tag{7}$$

$\Delta^0 H^{\mathrm{st}}(T_0)$ so derived for all $M$N nitrides are plotted in Fig. 5 with a dashed line labeled (a). In the same figure we show (filled symbols) $\Delta^0 H^{\mathrm{st}}(T_0)$ for ZrN, NbN, and MoN obtained from experimental information in Sec. III. The $\Delta^0 H^{\mathrm{st}}(T_0)$ given by Eq. (7) are considerably more negative than the directly measured values for ZrN and NbN and the extrapolated value for MoN. We conclude that using Eq. (7) leads to poor predictions of $\Delta^0 H^{\mathrm{st}}(T_0)$.

Guided by the preceding analysis of the sources of error in $E^{\mathrm{th}}_{\mathrm{coh}}$ we consider instead the quantity $\Delta E_{\mathrm{coh}} \equiv E_{\mathrm{coh}}(M\mathrm{C}) - E_{\mathrm{coh}}(M\mathrm{N})$. It follows from Sec. V A that most of the systematic part of the error in the theoretical results is expected to cancel in $\Delta E_{\mathrm{coh}}$. Further, $\Delta E_{\mathrm{coh}}$ is independent of the total energy of the transition-metal atom $E_M$, which should reduce the nonsystematic part of the error significantly. Therefore we expect the theoretical values for $\Delta E_{\mathrm{coh}}$ ($\Delta E^{\mathrm{th}}_{\mathrm{coh}}$) to give not only the right trend, but to account accurately for the thermodynamic ($\Delta E^{e}_{\mathrm{coh}}$) results. This expectation is tested in Fig. 6 where thermodynamic $\Delta E^{e}_{\mathrm{coh}}$ values are available for Zr, Nb, and Mo. The discrepancy between theoretical and thermodynamic values is 1, 9, and 11 mRy/atom, respectively, which is of the order of magnitude of the uncertainty in some of the $E^{e}_{\mathrm{coh}}$ values in Tables I and II. In Fig. 7 we extend the comparison to the corresponding compounds of the 3$d$ transition metals, using the results of our recent[3] study. The difference between $\Delta E^{\mathrm{th}}_{\mathrm{coh}}$ and $\Delta E^{e}_{\mathrm{coh}}$ is large for Cr compounds, and the reader is referred to our discussion[3] of the larger discrepancy between theory and experiments found for CrN. For the remaining elements to the right of Sc, the average discrepancy between theoretical and thermodynamic $\Delta E_{\mathrm{coh}}$ values is 5 (± 7) mRy/atom, which is in line with the results in Fig. 6.

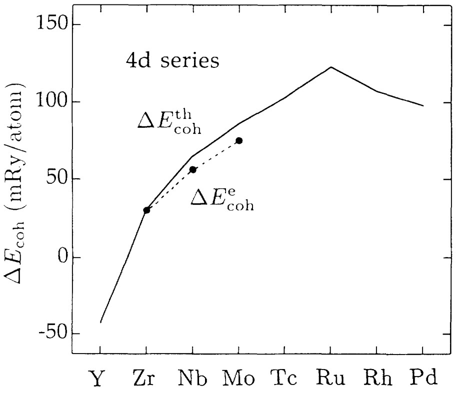

FIG. 6. The cohesive energy difference $\Delta E_{\mathrm{coh}} = E_{\mathrm{coh}}(M\mathrm{C}) - E_{\mathrm{coh}}(M\mathrm{N})$ for NaCl-type structure compounds plotted as a function of the position of the metal $M$ in the Periodic Table. The solid line labeled $\Delta E^{\mathrm{th}}_{\mathrm{coh}}$ refers to the difference between theoretical cohesive energies, and the solid symbols connected by the dashed line labeled $\Delta E^{e}_{\mathrm{coh}}$ to differences based on thermodynamic information.

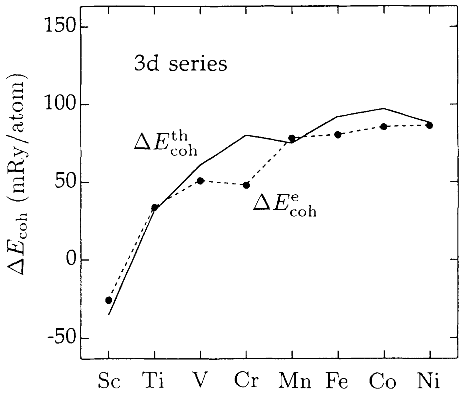

FIG. 7. The cohesive energy differences $\Delta E^{\mathrm{th}}_{\mathrm{coh}}$ and $\Delta E^{e}_{\mathrm{coh}}$, as in Fig. 6, for the NaCl-type structure carbides and nitrides of the 3$d$-transition-metal series according to the theoretical and thermodynamic values reported by Häglund *et al.* (Ref. 3).

In view of the good agreement between $\Delta E^{\mathrm{th}}_{\mathrm{coh}}$ and $\Delta E^{e}_{\mathrm{coh}}$ observed for the compounds for which experimental information is available, we apply the approximation

$$\Delta E^{e}_{\mathrm{coh}} = \Delta E^{\mathrm{th}}_{\mathrm{coh}} \tag{8}$$

to calculate $\Delta^0 H^{\mathrm{st}}(T_0)$ for all $M$N nitrides of the 4$d$ series relying on the $E^{e}_{\mathrm{coh}}$ values obtained in Sec. III. Our predictions for YN, TcN, RuN, RhN, and PdN are based on the $\Delta E_{\mathrm{coh}}$ values (in mRy/atom) 43, 103, 123, 107, and 98, respectively. The resulting $\Delta^0 H^{\mathrm{st}}(T_0)$ values are plotted in Fig. 5 using empty symbols connected by a solid line [labeled (b)]. The predicted values for ZrN, NbN, and MoN now differ from experiments by only 2, 11, and 15 kJ/mol of atoms, which compares well with the estimated uncertainties given in Tables I and II. For YN, previous compilations of thermodynamic data[33,34] give $\Delta^0 H^{\mathrm{st}}(T_0) = -150$ kJ/mol of atoms, which originates in an early estimate[35] based on interpolating between measurements for nitrides of other metals. The predictive method introduced here leads to a more negative $\Delta^0 H^{\mathrm{st}}(T_0)$. Lacking enthalpy information for the remaining nitrides of the series, we shall compare our predictions with independent estimates based on the interpolation scheme of Miedema and co-workers.[5]

### C. Comparison with the approach to $\Delta^0 H$ of Miedema and co-workers

Miedema and co-workers[5] have developed a semiempirical method to predict enthalpies of formation, $\Delta^0 H^{\mathrm{Mie}}$, of compounds. The method has been highly successful, but the theoretical reason for this is not well understood.[36] In the method of Miedema and co-workers,

$\Delta^0H^{\rm Mie}$ is calculated from an expression where each element is described by two parameters, representing an electronegativity and an electron density. These parameters are determined empirically through a "best fit" to known $\Delta^0H$ values, and partly through a consideration of phase-diagram information. Therefore the parameters for the 4*d* transition metals *M*, for C and for N, are partly based on the same experimental data as we use. However, the parameter values for C and N are also influenced by other carbides and nitrides, and similarly the parameters for the 4*d* metals *M* are influenced by compounds with S, P, etc. Further the method of Miedema and co-workers does not distinguish between different crystal structures of the same composition, and the entropy part in the Gibbs energy is not explicitly accounted for, as we do when treating high-temperature data.

In Fig. 8 we compare the present $\Delta^0H^{\rm st}(T_0)$ with $\Delta^0H^{\rm Mie}$, which are plotted as stars. Among our results one can distinguish $\Delta^0H^{\rm st}(T_0)$ values with three different origins. First we have the values corresponding to the stable carbides and nitrides of Zr and Nb, which are obtained by combining direct measurements. A second group includes the enthalpies for stable (YC) and metastable (MoC, MoN, TcC, RuC, RhC, and PdC) compounds that we derived by purely thermodynamic methods. The third group consists of $\Delta^0H^{\rm st}(T_0)$ values for YN, TcN, RuN, RhN, and PdN that were estimated in the preceding section. The fact that $\Delta^0H^{\rm Mie}$ agrees with the results from the first group is not unexpected, and means that our database of assessed information is consistent with that used by Miedema and co-workers. This makes a comparison between $\Delta^0H^{\rm Mie}$ and the two other groups of $\Delta^0H$ values presented here meaningful and most interesting. A significant discrepancy is found for YC, which may at least partly be due to a different account of the entropy part in the Gibbs energy of this compound. However, there is a very good agreement between $\Delta^0H^{\rm Mie}$ and our thermodynamic extrapolations for the metastable compounds of the second group. Finally, we note that the parameters of Miedema and co-workers make use of no thermodynamic information on metastable compounds, whereas our predictions for the third group of nitrides are based on values for metastable carbides and the theoretical $\Delta E_{\rm coh}$ quantity. In spite of that, for the metastable nitrides TcN, RuN, RhN, and PdN, $\Delta^0H^{\rm Mie}$ comes strikingly close to our results. This is another evidence of how well the method of Miedema and co-workers works. On the other hand, the basis of the method is empirical, which makes it difficult to assess its range of validity. The present work demonstrates that reliable predictions of $\Delta^0H^{\rm st}(T_0)$ can be obtained by combining two powerful approaches, the chemical thermodynamics of alloy systems and *ab initio* calculations of the electron band structure.

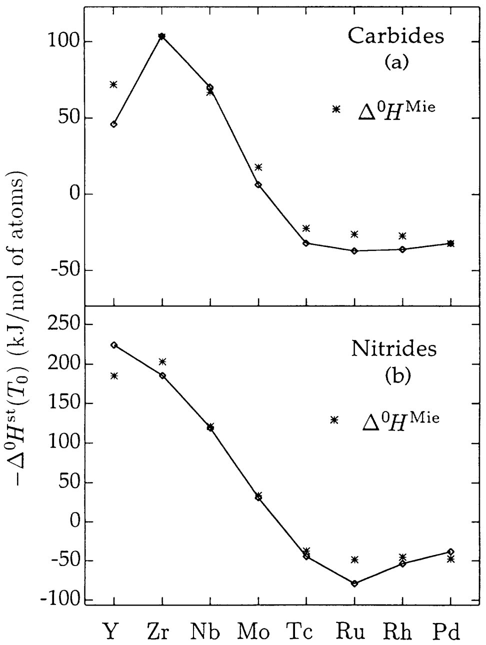

FIG. 8. The room-temperature enthalpy of formation, $\Delta^0H^{\rm st}(T_0)$ of (a) carbides and (b) nitrides of the 4*d* transition metals. Empty symbols connected by a solid line represent the values assessed from thermodynamic information in Sec. III or predicted in Sec. V B. Symbols denoted $\Delta^0H^{\rm Mie}$ refer to enthalpy-of-formation values given by the formula of Miedema and co-workers (Ref. 5).

## VI. COMMENTS ON APPLICATIONS IN MODELING OF PHASE DIAGRAMS

The phase diagram of an alloy system is sensitive to small differences in the Gibbs energy of the competing phases. For instance, the possibility of detecting a NaCl-type structure phase in the Cr-C system in a certain temperature range above $T_0$ (=298.15 K) depends on differences in *G* varying between 1 and 3 kJ/mol of atoms (0.8–2.3 mRy/atom).[37] This energy range is significantly lower than the probable uncertainty of the $\Delta^0H^{\rm st}(T_0)$ values predicted in the present work. However, we shall now show that our predictions still may have a role in the modeling of phase diagrams.

In Sec. III we referred to the two-sublattice thermodynamic model[25] for interstitial phases, and we explained how the application of such a model to, e.g., the solution of C (N) in the fcc structure of a metal *M* involves the evaluation of $\Delta^0H^{\rm st}(T_0)$ for a metastable *M*C (*M*N) compound, and of a regular-solution type of interaction parameter *L*. When this model was used to evaluate $\Delta^0H^{\rm st}(T_0)$ of metastable *M*C (*M*=Tc, Ru, Rh, Pd) compounds we treated *L* either as a free parameter determined in a fit to phase-diagram data (viz., for Tc-C and Pd-C), or we relied on the ideal-solution approximation, $L = 0$ (viz., for Ru-C and Rh-C). The largest error in the resulting $\Delta^0H^{\rm st}(T_0)$ due to the uncertainty in *L* was estimated as 9 kJ/mol of atoms by comparing with cases in Refs. 21 and 38 where more information is available. However, by applying the extrapolation procedure discussed in Sec. V B one may derive $\Delta^0H^{\rm st}(T_0)$ values with a comparable accuracy (Tables I and II) without recourse to phase-diagram fitting. This is expected to facilitate the current modeling work since it would lead to better defined *L* parameters in cases where the phase diagram information on the solution of C (N) in fcc $M$ is scarce. This should, in turn, make possible a meaningful study of the deviations from the ideal thermodynamic behavior in the interstitial phases based on transition metals.

## VII. CONCLUSIONS

We have performed *ab initio* calculations of the cohesive energies of $M$C and $M$N carbides and nitrides in the NaCl structure for $4d$ transition metals ($M$=Y, Zr, Nb, Mo, Tc, Ru, Rh, and Pd). For all of the carbides and for the nitrides ZrN, NbN, and MoN we have analyzed available thermodynamic information and obtained accurate values for their cohesive energies. This has allowed a detailed comparison between *ab initio* and experimental results. The trends in theoretical results are in excellent agreement with the thermodynamic values, but there is a positive difference between $E^{\mathrm{th}}_{\mathrm{coh}}$ and $E^{e}_{\mathrm{coh}}$ which varies between about 40 and 100 mRy/atom. We discuss the various contributions to the discrepancy, and argue why a major part of the errors in the theoretical calculation should cancel in the difference $\Delta E_{\mathrm{coh}} = E_{\mathrm{coh}}(M\mathrm{C}) - E_{\mathrm{coh}}(M\mathrm{N})$. In fact, the agreement between theory and experiment for $\Delta E_{\mathrm{coh}}$ is better than about 12 mRy for $M$=Zr, Nb, and Mo. This facilitates the estimation of cohesive energies for YN and the metastable TcN, RuN, RhN, and PdN, where we use thermodynamic values for the corresponding carbides in combination with the theoretical $\Delta E^{\mathrm{th}}_{\mathrm{coh}}$. We discuss how such a coupling between *ab initio* work and thermodynamic information can be used to provide new information, which is useful in the modeling of alloy phase diagrams. Enthalpies of formation calculated from the approach of Miedema and co-workers are in good agreement with the values derived by us.

## ACKNOWLEDGMENTS

We thank Thomas Jarlborg for commenting on this work and for letting us use his LMTO program. This work has partly been supported by the Swedish National Board for Industrial and Technical Development and the Swedish Natural Science Research Council.

---

[1] This is often referred to as the CALPHAD (i.e., calculation of phase diagrams) activity. Recent reviews of the models currently used in phase-diagram calculations have been given by I. Ansara, High Temp. Science **26**, 215 (1988/89), and B. Jönsson and B. Sundman, *ibid.* **26**, 263 (1988/89).

[2] A. Fernández Guillermet and G. Grimvall, Phys. Rev. B **40**, 10 582 (1989).

[3] J. Häglund, G. Grimvall, T. Jarlborg, and A. Fernández Guillermet, Phys. Rev. B **43**, 14 400 (1991).

[4] C. D. Gelatt, Jr., A. R. Williams, and V. L. Moruzzi, Phys. Rev. B **27**, 2005 (1983).

[5] F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema, and A. K. Niessen, *Cohesion in Metals* (North-Holland, Amsterdam, 1988).

[6] G. W. Fernando, R. E. Watson, M. Weinert, Y. J. Wang, and J. W. Davenport, Phys. Rev. B **41**, 11 813 (1990).

[7] N. Saunders, A. P. Miodownik, and A. T. Dinsdale, CALPHAD **12**, 351 (1988).

[8] G. Grimvall, M. Thiessen, and A. Fernández Guillermet, Phys. Rev. B **36**, 7816 (1987).

[9] A. Fernández Guillermet and M. Hillert, CALPHAD **12**, 377 (1988).

[10] T. Jarlborg and G. Arbman, J. Phys. F **6**, 189 (1976); **7**, 1635 (1977); G. Arbman and T. Jarlborg, Solid State Commun. **26**, 857 (1978).

[11] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Metals Park, Ohio, 1973).

[12] Scientific Group Thermodata Europe (SGTE), Data for Pure Elements, compiled by A. T. Dinsdale, NPL Report No. DMA(A) 195 (National Physical Lab., Teddington, UK, 1989) (unpublished).

[13] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data **14**, Suppl. 1 (1985).

[14] A. Fernández Guillermet, High Temp.-High Press. **19**, 119 (1987).

[15] A. Fernández Guillermet, Int. J. Thermophys. **6**, 367 (1985).

[16] A. Fernández Guillermet and G. Grimvall, Phys. Rev. B **40**, 1521 (1989).

[17] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys* (American Society for Metals, Metals Park, Ohio, 1973).

[18] D. Garvin, Bull. Alloy Phase Diagrams **2**, 262 (1981).

[19] L. Brewer, Rev. Lawrence Berkeley Laboratory Report No. LBL-3720 (unpublished).

[20] M. H. Rand (unpublished).

[21] A. Fernández Guillermet and G. Grimvall, J. Phys. Chem. Solids **53**, 105 (1992).

[22] All thermodynamic calculations reported in the present work were made using the Thermo-Calc system, described by B. Sundman, B. Jansson and J-O. Andersson, CALPHAD **9**, 153 (1985).

[23] J. Rosén and G. Grimvall, Phys. Rev. B **27**, 7199 (1983).

[24] A. Fernández Guillermet and G. Grimvall, J. Less-Common Met. **169**, 257 (1991).

[25] M. Hillert and L-I. Staffansson, Acta Chem. Scand. **24**, 3618 (1970).

[26] Using a computer program for the optimization of thermodynamic model parameters developed by B. Jansson, Ph.D. thesis, The Royal Institute of Technology, Stockholm, Sweden, 1984.

[27] A. Fernández Guillermet (unpublished).

[28] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol I.

[29] U. von Barth, Phys. Rev. A **20**, 1693 (1979).

[30] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circ. No. NSRDS-NBS35 (U.S. GPO, Washington, D.C., 1971).

[31] J. Häglund (unpublished).

[32] P. Bagno, O. Jepsen, and O. Gunnarsson, Phys. Rev. B **40**, 1997 (1989).

[33] O. Kubaschewski and C. B. Alcock, *Metallurgical Thermo-*

*chemistry*, 5th ed. (Pergamon, Oxford, 1979).

[34] L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, in *The Chemistry and Metallurgy of Miscellaneous Materials-Thermodynamics*, edited by L. L. Quill (McGraw-Hill, New York, 1950), p. 40.

[35] B. Neumann, C. Kröger, and H. Kunz, Z. Anorg. Allg. Chem. **218**, 379 (1934).

[36] D. G. Pettifor, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1987), Vol. 40, p. 43.

[37] A. Fernández Guillermet and G. Grimvall, Z. Metallkd. **81**, 521 (1990).

[38] A. Fernández Guillermet and K. Frisk, Int. J. Thermophys. **12**, 417 (1991); A. Fernández Guillermet and S. Jonsson, Z. Metallkd. **83**, 21 (1992).

[39] H. W. King, Bull. Alloy Phase Diagrams **2**, 528 (1982).

[40] F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, J. Am. Chem. Soc. **80**, 4499 (1958).

[41] E. K. Storms, High Temp. Sci. **3**, 99 (1971).

[42] C. P. Kempter and R. J. Fries, Analyt. Chem. **33**, 570 (1960).

[43] F. B. Baker, E. K. Storms, and C. E. Holley, Jr., J. Chem. Eng. Data **14**, 244 (1969).

[44] P. Roedhammer, W. Weber, E. Gmelin, and K. H. Rieder, J. Chem. Phys. **64**, 581 (1976).

[45] G. Grimvall and J. Rosén, Int. J. Thermophys. **4**, 139 (1983); G. Grimvall and M. Thiessen, in *Science of Hard Materials*, edited by E. A. Almond, C. A. Brookes, and R. Warren, IOP Conf. Proc. Ser. No. 75 (Institute of Physics and Physical Society, Bristol, 1986), p. 61; G. Grimvall, High Temp.-High Press. **17**, 607 (1985).

[46] C. P. Kempter, E. K. Storms, and R. J. Fries, J. Chem. Phys. **33**, 1873 (1960).

[47] L. Ramqvist, Jernkontorets Ann. **152**, 465 (1968).

[48] E. J. Huber, Jr., E. L. Head, C. E. Holley, Jr., E. K. Storms, and N. H. Krikorian, J. Phys. Chem. **65**, 1846 (1961).

[49] L. E. Toth, M. Ishikawa, and Y. A. Chang, Acta Metall. **16**, 1183 (1968).

[50] R. H. Willens and E. Buehler, Appl. Phys. Lett. **7**, 25 (1961).

[51] J-O. Andersson, CALPHAD **12**, 1 (1988).

[52] W. Trzebiatowski and J. Rudzinski, Z. Chem. **2**, 158 (1962).

[53] A. L. Giorgi and E. G. Szklarz, J. Less-Common Met. **11**, 455 (1966).

[54] H. R. Haines, P. G. Mardon, and P. E. Potter, in *Plutonium 1975 and Other Actinides*, edited by H. Blank and R. Lindner (North-Holland, Amsterdam, 1976), p. 233.

[55] V. N. Eremenko, T. Ya. Velikanova, and A. A. Bondar, Sov. Powder Metall Met. Ceram. **28**, 868 (1989).

[56] *Binary Alloy Phase Diagrams*, 2nd ed., edited by T. B. Massalski, H. Okamoto, P. R. Subramanian, and L. Kacprzak (American Society for Metals, Metals Park, Ohio, 1990).

[57] Y. J. Bhatt, R. Venkataramani, and S. P. Garg, J. Less-Common Met. **132**, L21 (1987).

[58] W. Huang, Scand. J. Metall. **19**, 26 (1990).

[59] P. Gustafson, Scand. J. Metall. **14**, 259 (1985).

[60] A. Fernández Guillermet, Z. Metallkd. **78**, 700 (1987).

[61] R. H. Siller, W. A. Oates, and R. B. McLellan, J. Less-Common Met. **16**, 71 (1968).

[62] P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (American Society for Metals, Metals Park, Ohio, 1985).

[63] E. Rudy and F. Benesovsky, Monatshf. Chem. **92**, 415 (1961).

[64] A. D. Mah and N. L. Gellert, J. Am. Chem. Soc. **78**, 3261 (1956).

[65] E. I. Gal'braikh, O. P. Kulik, A. A. Kuznetsov, M. D. Lyutaya, and M. P. Morozova, Sov. Powder Metall Met. Ceram. **9** (93), 748 (1970).

[66] E. J. Huber, Jr., E. L. Head, and C. E. Holley, Jr., J. Phys. Chem. **68**, 3040 (1964).

[67] L. E. Toth, *Transition Metal Carbides and Nitrides* (Academic, New York, 1971).

[68] G. Brauer and H. Kirner, Z. Anorg. Allg. Chem. **328**, 34 (1964).

[69] P. Ettmayer, Monatshf. Chem. **101**, 127 (1970).

[70] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, London, 1967), Vol. II.

[71] G. Linker, R. Smithey, and O. Meyer, J. Phys. F **14**, L115 (1984).

[72] K. Frisk, CALPHAD **15**, 83 (1991).

[73] W. Trzebiatowski and J. Rudzinski, J. Less-Common Met. **6**, 244 (1964).